

THE OXIDATION OF FUEL OIL #6 STUDIED BY
DIFFERENTIAL SCANNING CALORIMETRY

By

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INTRODUCTION

The studies on combustion of heavy fuel oil are important because of the extended use of this fuel as an energy source for the production of electricity. With the continuous increase in the extraction of products from crude oil, there exists a continuous degradation in the quality of the residue that is to be burned in a utility boiler. The degradation of the quality in the residual oil, means a higher sulfur content in the fuel, higher aromaticity, and higher asphaltene and metallic content. Some of these species, yield products of combustion which are aggressive to both the environment, and some of the components within the boiler. It is believed (1) that an understanding of why and how pollutants form, must come from an understanding of the chemical kinetics in the flame. That is, in order to protect the environment, and increase the availability of a large boiler more research is needed to understand the chemistry of oxidation of complex fuel mixtures.

Various authors (2-6) have pointed out the potentiality of the different techniques in thermal analysis for the characterization of petroleum products and coal. However, very little kinetic information has been extracted from the studies which involve the use of thermoanalytical techniques. The chemical kinetics of thermo-oxidative processes in fuels, may contribute to a large extent to the understanding of the chemistry

of oxidation of such mixtures. Weber (2), has reported the potential utilization of differential thermal analysis (DTA) to obtain kinetic parameters for the oxidation of hydrocarbons. He concluded, though, that for the kinetics of oxidation of heavy fuel oil no theory for DTA could yet be used, because of the complexity of the thermograms. Adonyi (3), has shown that kinetics may be obtained for petroleum products by means of DTA, and thermogravimetric techniques (TG). More recently, Noel and Cranton (4), have measured the activation energy, E_a , for the oxidation of lube oil by differential scanning calorimetry (DSC). These authors make the observation that more research is necessary in order to have a better understanding of the results observed by DSC. Smith et al. (7), have used TG to measure the rate, and the E_a for the oxidation of sixty-six coal samples. Valayavin et al. (8), utilized TG to study the thermolysis of high molecular weight petroleum residues, and established a reaction rate law as a function of the viscosity of the medium and a diffusion parameter.

In the present work, we have utilized DSC to study the thermal oxidation of four samples of Mexican fuel oil. We have also obtained kinetic parameters such as the overall activation energy for the oxidation of the fuel at low temperature (200 - 550°C).

EXPERIMENTAL

The experimentation was carried out by means of a DuPont Thermal Analyzer Model 990 with its standard DSC attachment. The instrument was calibrated with Indium. The temperature was varied from 20 to 550°C with a scanning rate of 10°C/min. The sensitivities used were 20 and 50 mV/cm. The sample and reference pans were made of aluminum, and the sample weight was kept at around 2 mg. Four different samples of Mexican fuel oil # 6 were analyzed, and the experiments were performed with a constant flow of nitrogen, oxygen or a mixture of both. The flow rates, and the O_2/N_2 ratios utilized

throughout the experiments are shown in Table 1.

RESULTS AND DISCUSSION

Experiments with pure nitrogen flow did not show any endothermic reaction, but a gradual displacement from the base line, especially above 300°C. This displacement indicates that the evaporation of some compounds in the fuel has occurred. A residue was observed in the sample pan after the run was completed. Figure 1 shows a typical thermogram obtained with pure oxygen flow. This thermogram is very similar to those shown in the literature for tar sands (2), or high asphaltene crude oil (9), which may show the quality or the characteristics of the fuel. Indeed, the fuel studied here has a > 10% asphaltene content, and > 3% sulfur. In figure 1, it is observed a small exothermic reaction zone (zone 1) at ~ 300°C, and a larger zone (zone 2), also exothermic, which starts at ~ 400°C. Several small peaks are shown at the low temperature side of the second zone. It is also observed a rapid fall-off of the signal after the maximum has been reached. All the sample was consumed during the experiments with high oxygen concentration in the gas flow. Figure 2, presents a thermogram obtained with a low oxygen concentration in the gas flow. It is observed that the reaction zone is shifted towards higher temperatures.

From the calibration of the instrument with In, it was calculated that the sensitivity of 20 mV/cm corresponded to 43.5 mcal/min-cm. Table 2 shows the results for the heat of reaction measured for both exothermic zones in the thermograms. The values in Table 2 range from as high as 3.3 Kcal/g for the experiments with pure O₂, to as low as 1.4 Kcal/g for the experiments with a 1:9 O₂/N₂ ratio. These values for the heat of reaction, are low if they are compared with the usual heat content of these fuels, which is ~ 10 Kcal/g. Other reports (4), have also measured similar heats of reaction to those reported here, and utilizing a similar

technique. The difference between our values, and the value of 10 Kcal/g for the heat content of the fuel are explained as follows: 1) First, we have a flow system in which we are continuously carrying away heat from the reaction envelope. 2) Second, most probably, we do not have a complete oxidation of the fuel. That is, we do not have a complete adiabatic combustion-type of experiment from which the heat content of the fuel is normally evaluated. It must be observed, that the extreme values for the heat of reaction in table 2 were obtained for experiments with approximately the same total flow. The only difference among both experiments is the oxygen concentration. Similar features were observed in other investigations where TG and DTA were used (2,9), and in which the pressure of air inside the reaction device was varied. That is, the actual oxygen concentration, and availability for the fuel was varied. We may conclude that different reaction channels are being followed according to the oxygen concentration. Hence, different heats of reaction are measured for the experiments with pure O_2 , and for experiments with a 1:9 O_2/N_2 ratio.

In order to obtain kinetics parameters from the thermograms, we utilized the theory of Borchardt and Daniels (10). The zones I and II in the thermograms were treated independently, and it was assumed a reaction of pseudo-first order. A pseudo-first order kinetics implies a first order reaction with respect to the fuel, and a constant oxygen concentration. The latter assumption is clearly justified for the experiments with a high oxygen content in the gas flow. A first order reaction with respect to the fuel may be justified through the results. Figure 3 and 4 show the Arrhenius plot for the zone I of the thermograms. The results in figure 3 are for the experiments with pure oxygen; whereas those in figure 4 present the experiments with low concentrations of O_2 in the gas flow. For the data in figure 3 it is possible to draw two different straight lines. Thus, two different activation energies are obtained, one of 12 ± 1 Kcal/mol, and a higher one of 22 ± 1 Kcal/mol. From the data

in figure 4, only one activation energy has been obtained with a value of 16 ± 1 Kcal/mol. The lower value for E_a in the experiments with pure O_2 occurs at the higher temperatures of zone I in the thermograms. Thus, it is possible that diffusion controlled reactions occur at these temperatures. In fact, it has been found (8) that, the thermolysis of petroleum residues in a TG experiment is highly influenced by diffusion processes. The results in figure 4, along with the results of the heat of reaction for the experiments with a poor oxygen concentration, indicate that a different reaction scheme is being followed. This last statement should be supported by the identification of the reaction products.

Figures 5 and 6 show the results for zone II in the thermograms. Figure 5 presents the results for the pure O_2 experiments, and figure 6 presents the data for the experiments with a low oxygen concentration. In this case, we only obtain one activation energy for the pure oxygen data (figure 5) $E_a = 36 \pm 1$ Kcal/mol. In figure 6 we observe a straight line only for the experiments with a 1:3 O_2/N_2 ratio, and gas flows of 41 ml/min and 87 ml/min. The rest of the data points in figure 6 show large deviations from a straight line. These deviations in the experiments, with the lowest oxygen concentration in the gas flow, seem to indicate that we may no longer assume a pseudo-first order kinetics.

The various techniques in thermal analysis, may be very useful to obtain an overall view of the oxidation reactions for mixtures as complex as the heavy fuel oil. This overall picture, may include quantitative information such as activation energies. In general, we believe that these studies may serve as a basis to understand more complex oxidation reactions such as those occurring within a flame.

ACKNOWLEDGMENTS

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TABLE 2
HEAT OF REACTION

SAMPLE	FLOW (ml/min)	RATIO O ₂ :N ₂	ZONE I (Kcal/g)	ZONE II (Kcal/g)
#1	90	1:0	0.4	1.9
#2	90	1:0	0.6	2.5
#3	90	1:0	0.5	2.5
#4	98	1:0	0.5	2.7
#4	89	1:1	0.3	1.8
#4	87	1:3	0.2	1.6
#4	91	1:9	0.2	1.2
#4	41	1:3	0.3	1.6
#4	24	1:3	0.2	1.4

TABLE 1
EXPERIMENTAL FLOW CONDITIONS

FLOW (ML /MIN)	GAS	RATIO $O_2:N_2$
90-100	N_2	0:1
90-100	O_2	1:0
85-90	O_2/N_2	1:1
85-90	O_2/N_2	1:3
40	O_2/N_2	1:3
24	O_2/N_2	1:3
11	O_2/N_2	1:3
90	O_2/N_2	1:9

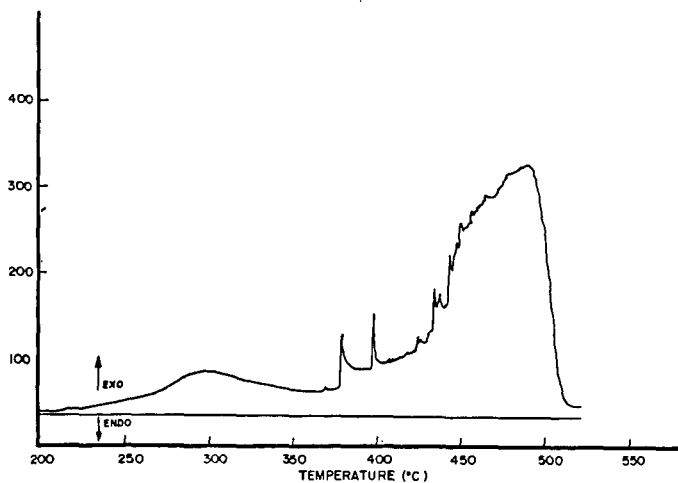


Figure 1. Sample #4. Atmosphere: pure oxygen.
Total flux: 98 ml/min.

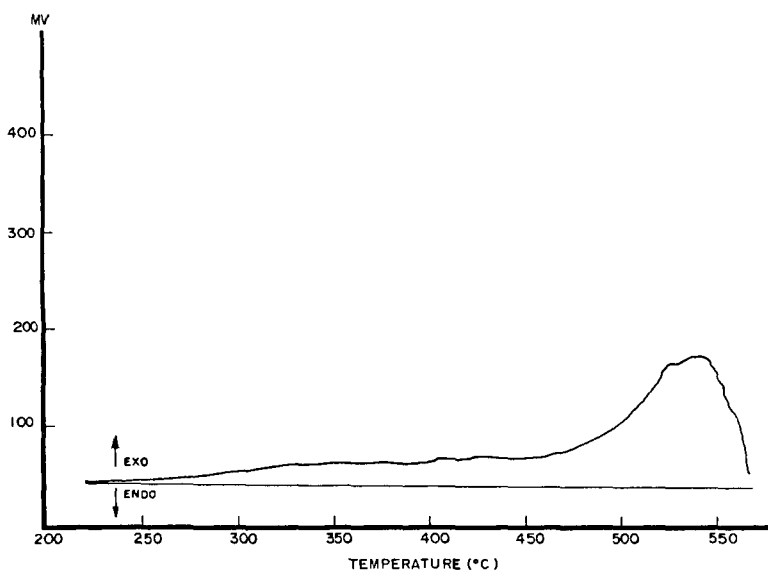


Figure 2. Sample #4. Atmosphere: O_2/N_2 (1:9).
Total flux: 91 ml/min.

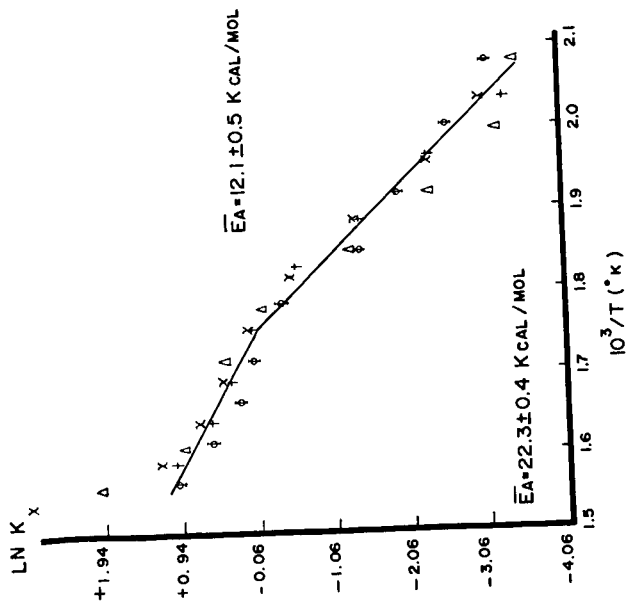


Figure 3. Arrhenius plot for experiments with pure oxygen. Zone I.

- Δ Sample #1 (O₂ = 90 ml/min)
- φ Sample #2 (O₂ = 90 ml/min)
- + Sample #3 (O₂ = 90 ml/min)
- x Sample #4 (O₂ = 98 ml/min)

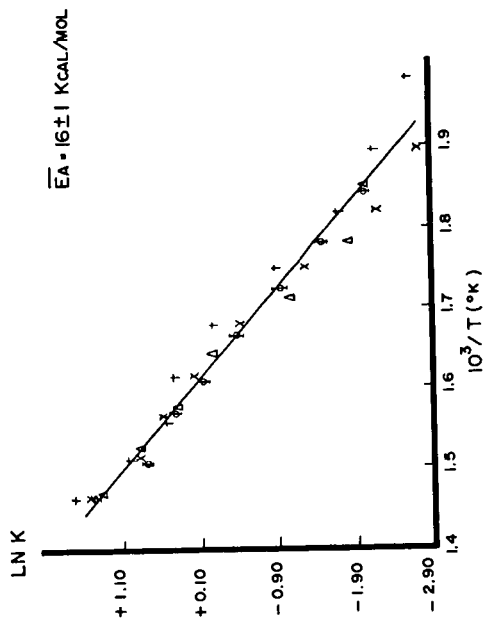


Figure 4. Arrhenius plot for experiment with low oxygen concentration Zona I. Sample #4.

- x 1:3 O₂/N₂ (87 ml/min)
- + 1:3 O₂/N₂ (41 ml/min)
- φ 1:3 O₂/N₂ (24 ml/min)
- Δ 1:9 O₂/N₂ (91 ml/min)

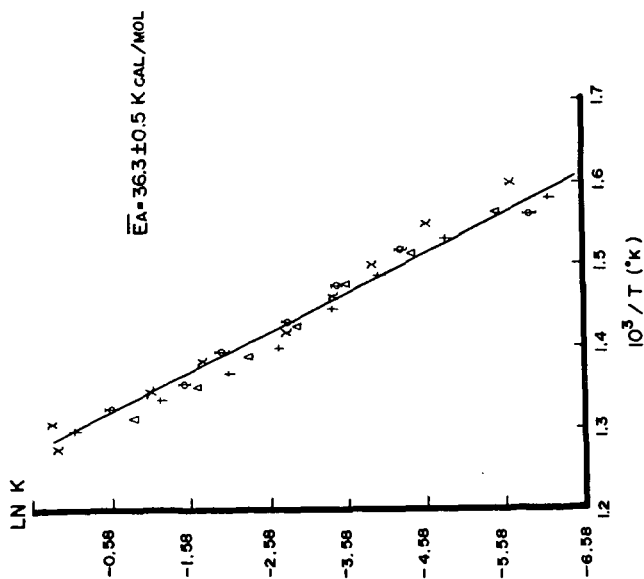


Figure 5. Arrhenius plot for experiments with pure oxygen. Zone II.
 Δ Sample #1 ($O_2 = 90 \text{ ml/min}$)
 ϕ Sample #2 ($O_2 = 90 \text{ ml/min}$)
 $+$ Sample #3 ($O_2 = 90 \text{ ml/min}$)
 \times Sample #4 ($O_2 = 98 \text{ ml/min}$)

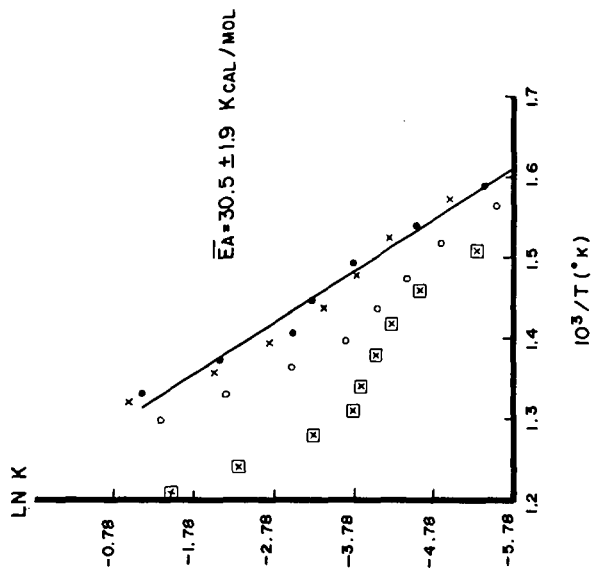


Figure 6. Arrhenius plot for experiments with low oxygen concentration. Zone II. Sample #4.
 \times 1:3 O_2/N_2 (87 ml/min)
 \bullet 1:3 O_2/N_2 (41 ml/min)
 \square 1:3 O_2/N_2 (24 ml/min)
 \circ 1:9 O_2/N_2 (91 ml/min)